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VAPOR-PRESSURE CHART FOR VOLATILE HYDROCARBONS[1/]

By R. Vincent Smith[2/]

INTRODUCTION

While studying the physical properties of petroleums and natural gases, particularly the fractional distillation of petroleum oils and natural gases in the laboratories of the Bureau of Mines, Bartlesville, Okla., the writer frequently had to refer to published data on the vapor pressures of volatile hydrocarbons. As such data are scattered widely throughout the literature, often not readily available, and frequently referred to uncommon units of pressure and temperature, an attempt was made to collect them, refer them to commonly used units of pressure and temperature, and arrange them on a chart that could be used conveniently in the laboratory. A copy of the writer's chart is included, as it is the nucleus of this report. The ranges of pressures and temperatures are those commonly used in studies requiring data on vapor pressures and boiling points of hydrocarbons from methane to n-dodecane.

In constructing the chart, many data were taken from already compiled sources (19, 21, 23, 24, 25, 28, 36, 43, 44),[3/] but wherever possible the data were compared and checked with the original before they were used to interpolate and extrapolate the vapor-pressure curves.

ACKNOWLEDGMENTS

The investigation reported here was made under the general supervision of R. A. Cattell, chief engineer, Petroleum and Natural Gas Division, Bureau of Mines, Washington, D. C., and N. A. C. Smith, supervising engineer, Petroleum Experiment Station, Bartlesville, Okla. The work was carried out

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1/ The Bureau of Mines will welcome reprinting of this paper, providing the following footnote acknowledgment is used: "Reprinted from Bureau of Mines Information Circular 7215."

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3/ Numbers in parentheses refer to citations in the bibliography at the end of this report. Page references represent those in the citation.

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under the direct supervision of Kenneth Eilerts, physical chemist, and R. E. Heithecker, senior petroleum engineer, Bureau of Mines, Bartlesville, Okla.

The vapor-pressure chart was prepared by S. B. Thomas. The manuscript was read and criticised by the following members of the Bureau of Mines: E. S. Burnett, C. B. Carpenter, Kenneth Eilerts, H. C. Miller, M. A. Schellhardt, and Gustav Wade. To them the writer is deeply indebted.

DISCUSSION OF VAPOR PRESSURE

When the vapor of a single component liquid is exposed to "free" space above it there is a continuous movement of the molecules of the liquid from the surface of the liquid into the "free" space, and at the same time a continuous passing of molecules of the vapor into the liquid. If these two phenomena exactly balance one another, the liquid and its vapor will be in equilibrium, and the vapor will be saturated with liquid. The resultant pressure exerted by the saturated vapor is known as its vapor pressure.

Vapor pressures of single component liquids are independent of the quantities of vapor or liquid in equilibrium but vary with temperature, and for every temperature below the critical pressure a definite pressure is exerted by a vapor in equilibrium with liquid.

Many vapor-pressure charts have as their basis the coordinates (logarithm of vapor pressure and reciprocal of absolute temperature) suggested by an integrated form of the Clausius-Clapeyron equation[4/], which is as follows:

$$\log p = -\frac{A}{T} + B,$$

where p = vapor pressure,
T = absolute temperature, and
A and B = constants.

Experimental data, however, do not yield straight lines when plotted upon this basis but yield curves in which the curvature is small throughout their extent. Consequently, the logarithm of pressure and the reciprocal of absolute temperature were chosen as coordinates for a convenient graphic means for presenting data on vapor pressures of hydrocarbons.

A vapor-pressure chart using a special nonuniform temperature scale has been suggested by Cox (16) in an effort to present vapor-pressure data as

4/ A derivation of the equation is given by Getman and Daniels (22).

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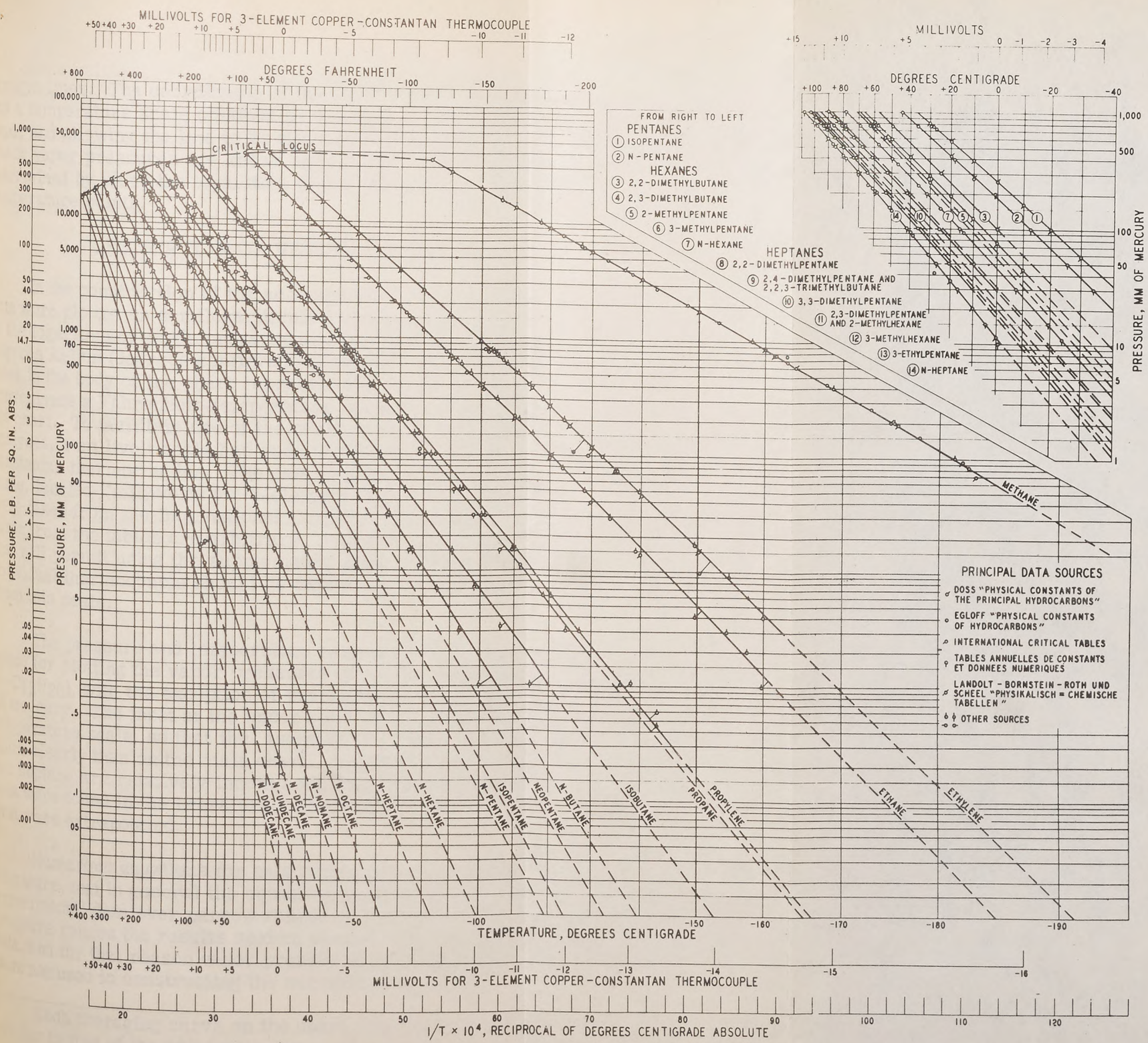

FIGURE 1. - VAPOR PRESSURES OF HYDROCARBONS

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straight lines. The coordinates of the chart are the logarithm of vapor pressure and a temperature scale obtained by drawing a straight line on semilogarithmic paper and allowing the line to be the vapor-pressure curve of some substance whose vapor pressures are known accurately. The temperature scale is determined by using the logarithm of the pressure to locate corresponding temperature points.

DESCRIPTION OF VAPOR-PRESSURE CHART

In the construction of the accompanying vapor-pressure chart, collected data were plotted on semilogarithmic coordinate paper, on which the ordinate is the logarithm of vapor pressure and the abscissa is the reciprocal of degrees Kelvin (degrees centigrade absolute). As finally drawn, the vertical lines in the body of the chart represent degrees centigrade, and for extra convenience a Fahrenheit-temperature scale has been placed at the top of the chart. To facilitate use of the chart in low-temperature distillation analyses, a millivolt scale has been provided for users of 3-element copper-constantan thermocouples. The data required to construct the temperature scale, labeled "millivolts for 3-element copper-constantan thermocouple," were taken from the International Critical Tables (25). Although the values taken from the tables are arbitrary, matched couple pairs may be obtained that will permit using the supplemental scale. For precise work, each individual thermocouple should be calibrated to determine individual deviations from this scale.

The pressure and temperature ranges covered by the chart provide space for plotting the vapor pressures of all the hydrocarbons up to n-dodecane ($n\text{-}C_{12}H_{26}$), with the exception of pressures for methane below 15 millimeters of mercury. The inset at the upper right of the chart has an expanded temperature scale, so that the isomers of hexane and heptane could be shown more clearly than on the main chart. Available data for the isomers of hexane and heptane are relatively incomplete, and only the normal boiling-point data were found in the literature. Accordingly, dashed curves are used where data were extrapolated.

Numerous equations for calculating vapor pressures were found in the literature, and in general the equations yielded results that agreed with the experimental data over narrow ranges of pressure; over more extensive pressure ranges the results seldom agreed with the experimentally determined data, and for that reason vapor pressures calculated by means of equations were not used in constructing the accompanying chart.

Each averaging curve on the chart was drawn so that its shape was similar to that of the adjacent curves. Normal boiling-point data given by

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Egloff (21), which are weighted averages of all available experimental data, were given the most consideration in determining the position of the curves. Many of the data for pressures above 1,000 millimeters of mercury were taken from Tables annuelles de constantes et donnees numeriques (44) and from the work by Young (48), who published the original data in connection with a study of the boiling points of the normal paraffin hydrocarbons. The close agreement between these and other data in the low-pressure range and data at higher pressures from other sources indicated that considerable weight could be given those data in determining the position of the averaging curves at high pressures.

The data available for determining the greater part of curves for methane (1, 19, 21, 24, 28, 36, 44, 48), ethylene (12, 14, 19, 21, 24, 27, 28, 32, 33, 36, 44), and ethane (1, 6, 10, 12, 14, 19, 21, 23, 24, 26, 28, 31, 32, 33, 35, 36, 37, 44, 48) were in close agreement. It was necessary, however, to extend the curves to low pressures, and the extrapolations (dashed part of the curves) were drawn to conform in shape with the adjacent curves.

There was good agreement among the published data for propylene (propene) (13, 14, 19, 21, 24, 27, 28, 33, 36, 38, 45) from different sources for pressures above 1,000 millimeters of mercury, and the curve for propylene was drawn parallel to the curve for propane, even though the curve did not pass through all the data points in the low-pressure range. Published data for propane (1, 8, 13, 14, 17, 19, 21, 23, 24, 28, 33, 36, 44, 48) do not agree exactly, and small differences were noted in the pressure range below 1,000 millimeters of mercury. The trend of the data, however, was consistent, and it was possible to draw a curve for propane with its position fixed within the limit of probable experimental errors.

The available data for insobutane (methyl-propane) (2, 14, 15, 17, 19, 21, 23, 24, 28, 36, 38) between mercury pressures of 300 and 760 millimeters were inconsistent in trend but regular at higher and lower pressures. Consequently, the averaging curve was drawn giving the least weight to data in the intermediate pressure range.

Two distinct curves for pressures greater than 1,000 millimeters of mercury were obtained when the data for n-butane (1, 4, 9, 13, 14, 15, 17, 19, 21, 23, 24, 28, 36, 38, 44, 48) were plotted. As the curve determined by the data reported by Young (48) conformed to data from other sources in the low-pressure range, the curve shown on the chart was drawn through one set of data without giving consideration to the other set.

The available vapor-pressure data for neopentane (2,2-dimethylpropane) (3, 19, 21, 43, 46) are complete only in the pressure range from 100 to 1,000

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millimeters of mercury, and although there are small differences between the values from the five sources, they are small and of the magnitude of experimental errors. The neopentane curve was extrapolated in both directions so as to correspond in shape with adjacent curves for n-butane and isopentane. The values of the critical constants for neopentane reported by Doss (19) and originally published by the Standard Alcohol Co. (43) are close to those of isopentane. Consequently, they do not conform to the trend of the vapor-pressure data, and it was concluded that an error exists either in the vapor-pressure data or in the critical pressure and temperature data, or in both. As the vapor pressure data for neopentane are from two sources that are in agreement, more confidence can be placed in the vapor-pressure data than in the reported critical-pressure and temperature data.

Published data for isopentane (19, 21, 24, 28), n-pentane (1, 19, 21, 24, 28, 39, 44, 47, 48), n-hexane (1, 19, 21, 24, 28, 29, 39, 42, 44, 47, 48), n-heptane (1, 7, 11, 19, 20, 21, 24, 26, 28, 29, 34, 39, 41, 42, 44, 47, 48), and n-octane (1, 19, 21, 24, 28, 29, 30, 39, 44, 47, 48) agree and permit determining the positions of the averaging curves with little doubt as to their correct position on the chart.

Most of the available data for n-nonane, n-decane, n-undecane, and n-dodecane were published by Young (48), and curves drawn through the plotted data are regular, consistent in trend, and agree with those based on data from other sources - (n-nonane, 1, 19, 21, 39, 44, 47, 48), (n-decane, 1, 19, 21, 28, 30, 39, 44, 47, 48), (n-undecane, 1, 19, 21, 39, 44, 47, 48), and (n-dodecane, 5, 19, 21, 39, 44, 47, 48).

The data on critical pressures and temperatures compiled by Doss (19) and Pickering (36) were used in the work reported here, as they were consistent with other data except for those given for 2,2-dimethylpropane (tetramethylmethane or neopentane) and n-decane.

The inset at the upper right of the chart is a plot of the available data for the insomers of hexane (11, 19, 21, 24, 28) and heptane (11, 19, 20, 21, 40). Data for 2,2-dimethylbutane (11, 19, 21, 24, 28), 2,3-dimethylbutane (11, 19, 21), 2,2,3-trimethylbutane (11, 19, 20, 21, 40), and 3-ethylpentane (11, 19, 20, 21) are complete between pressures of 100 and 1,000 millimeters of mercury but incomplete for the other isomers. Certain curves, therefore, have been indicated on the chart by dashed lines approximately parallel to the curves for closely related components on which complete data were available.

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CONCLUSION

The vapor-pressure chart (accompanying this report) of many volatile, naturally occurring hydrocarbons was prepared from data gleaned from a long list of references. The search of the literature revealed that vapor-pressure data are complete for the normal hydrocarbons up to and including n-decane ($n\text{-}C_{10}H_{22}$), with the exception of n-nonane ($n\text{-}C_9H_{20}$). Vapor- pressure data are incomplete for isopentane below pressures of 50 millimeters of mercury. The available critical constants for neopentane are apparently in error, and the vapor-pressure data, when plotted on the chart, yield 2 lines with slightly different slopes. Data for isobutane are inconsistent in trend between pressures of 300 and 760 millimeters of mercury.

Need exists for a set of empirical equations that have been fitted to experimental data and that would permit accurate calculation of vapor-pressure extrapolations and interpolations over the entire range of pressures. Such a set of equations would "round out" present knowledge of vapor pressures of hydrocarbons.

The accompanying vapor-pressure chart has been useful in distillation procedures where pressures and temperatures vary over wide ranges. The chart has been used successfully to determine "cut points" for distillations at pressures above atmospheric and for distillations at pressures below 50 millimeters of mercury.

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